Enaminones in the Synthesis of New Polyaza Heterocycles

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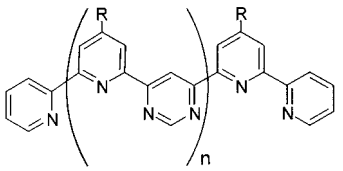
A simple and efficient method for the synthesis of larger polyaza heterocyclic structures **6a**, **6b** and **8** with 1,3-pyrimidine units has been developed, based on the reaction of enaminones with appropriate guanidines or carboxamidines under basic conditions. Using this procedure, several new, optically active polyaza heterocycles **10**, **12** and **13** have been prepared in good yields, from enantiomerically pure N_α-Boc-L-arginine as guanidine reagents.

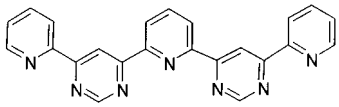
The use of polyaza heterocyclic ligands in self-assembly reactions involving metal ions has been a central theme in supramolecular chemistry.[1][2] As a consequence of the research in designing new systems, the synthesis of these heterocyclic structures has received special attention. Very recently, J.-M. Lehn et al.[3] described the synthesis of new polyaza heterocyclic structures such as **1** (Figure 1) containing pyridines and 1,3-pyrimidine units. Two different synthetic procedures were used: the first involved Pd^{II}-catalysed cross-coupling reactions (for $n = 2$); the second involved the combination of tin-mediated cross-coupling reactions, and Potts's synthesis (for $n = 3, 5$). Ligands **1** exist in (racemic) helical conformations in both the solid state and solution. These original ligands were used in the construction of ordered inorganic architectures by reaction with Ru(tpy)Cl_3 and Cobalt(II).[4] Steel et al.[5] reported the synthesis of a pentaheterocyclic ligand **2** (Figure 1) by a double Claisen condensation of ethyl dipicolinate with acetylpyridine, followed by the cyclization of a diketone intermediate, with formation of the two pyrimidine rings. The reaction of this polydentate ligand with Ru(bpy)$_2Cl_2$ as a metal fragment led to a dinuclear ruthenium complex, with tetrahedral coordination through the two terminal bipyridines. This work showed the importance of the design and synthesis of new and interesting polyaza heterocycles containing pyridine, and 1,3-pyrimidine units.

We have recently described a new procedure for the preparation of polyaza heterocycles containing pyridine and 1,3-pyrimidine units.[6] In this paper, we describe the extension of our method to the synthesis of larger polyaza heterocycles. By condensation of enaminones with N_α-Boc-L-arginine, as guanidine reagents, we obtained new polyaza heterocycles with chiral side arms.

Figure 1



1 n = 2; R = H
n = 3; R = S-nPr
n = 5; R = S-nPr



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Results and Discussion

In our previous paper, we reported that the reaction of bis(β-dimethylaminoenone) **3** with different carboxamidines under basic conditions led to the new tridentate ligands **4a**−**c** in good to high yields,[6] and the ligand **4d** was obtained in 95% isolated yield by condensation of **3** with 3 equivalents of *N*-ethylguanidine hydrochloride in the presence of 5 equivalents of sodium ethoxide under standard conditions (Scheme 1).

The first extension of this work concerns the preparation of the polypyridylpyrimidines by reaction of the bis(enaminone) **3** with pyridine and 2,2′-bipyridinecarboxamidines. Thus, the condensation of **3** with 2.5 equivalents of 2-pyridinecarboxamidine[7] and 4 equivalents of sodium ethoxide in boiling ethanol, resulted in the formation of the pentacyclic species **6a** in 90% yield (Scheme 2). This material was purified by column chromatography on alumina, and single crystals were obtained from chloroform/methanol. The

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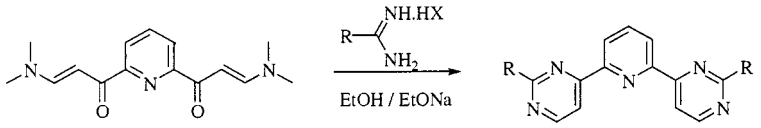
  1434−193X/98/1212−2907 $ 17.50+.50/0

Scheme 1



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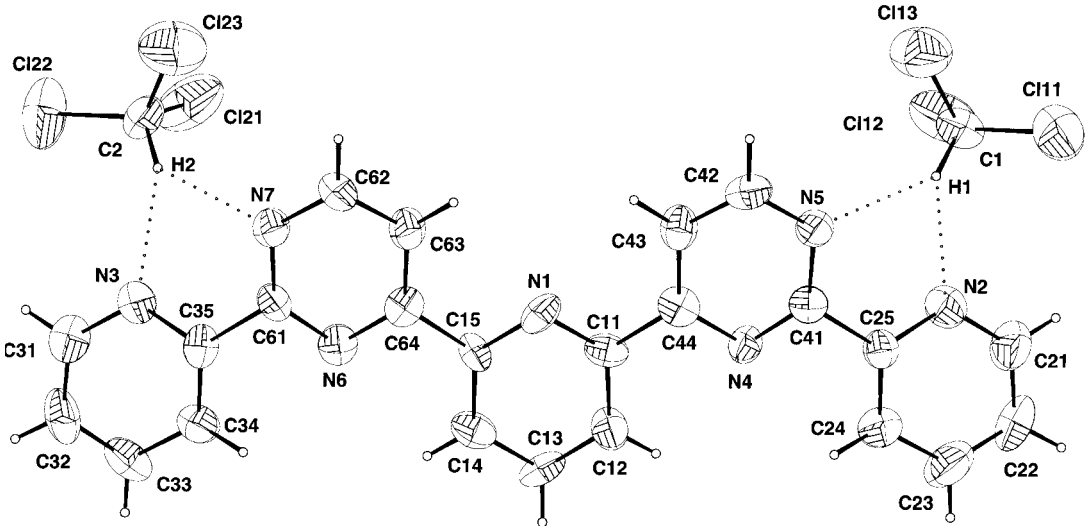
4a R = Me (90%)
4b R = NH_2 (90%)
4c R = H (50%)
4d R = NHEt (95%)

structure was then determined by X-ray diffraction. The molecular structure of **6a** with its atom labelling scheme is shown in Figure 2.

Figure 2. Molecular view of compound **6a** with atom-labelling scheme; ellipsoids represent 30% probability



The molecule has an essentially planar conformation. There are, however, slight distortions when going from the central pyridine to the external pyridine rings, with dihedral angles between these rings of 7.5(4)° and 5.4(4)°. As observed in other related molecules, the nitrogen N(1) of the central pyridine ring is *trans* with respect to nitrogen atoms N(4) and N(6) of the pyrimidine rings. It is known that such a conformation minimizes electronic repulsions between the lone pairs of the nitrogen atoms.[6] The nitrogen atoms of the terminal pyridine rings, however, are forced to be *cis* with respect to one of the nitrogen atoms of the pyrimidine rings. The molecules pack as closely stacked (3.34 Å interplanar spacing) aromatic layers roughly parallel to the 110 plane. It should be noted that two chloroform molecules of crystallization are located so that each makes close contacts with both N(2) (2.30 Å) and N(5) (2.32 Å) or N(3) (2.41 Å) and N(7) (2.33 Å), respectively. Although hydrogen-bonding interactions between the hydrogen atom of a chloroform molecule and a nitrogen atom is not unusual,[8] to the best of our knowledge, only one example of a bridging H interaction with two nitrogen atoms has been previously reported, and refers to an unsymmetrical bridge with H···N distances of 2.31 Å and 2.76 Å, respectively.[9] Very recently, a C−H···π-type and C−H···O-type interactions between chloroform and $(Me_3Si)C_4Si(OCH_2CH_2)_3N$ were described.[10] It is also noteworthy to relate a recent example concerning a bridging hydrogen interaction between one of the H atom of the methyl group of a toluene molecule and two nitrogen atoms of a naphthyridine molecule with rather long contacts of 2.76 Å and 2.83 Å.[11]

The molecule **6b**, which can be considered as a bis(bipyridine) equivalent, was obtained in 75% isolated yield by reaction of bis(enaminone) **5** and 2-pyridinecarboxamidine under the same conditions as for **6a** [the bis(enaminone) **5** was prepared from 1,3-diacetylbenzene and Bredereck reagents]. This material was purified by precipitation from cooled ethanol and single crystals were obtained from chloroform/methanol. The structure was then determined by X-ray diffraction. The molecular structure of **6b** with its atom labelling scheme is shown in Figure 3.

As for **6a**, the molecules of **6b** have an essentially planar conformation with somewhat larger distortions when going from the central phenyl ring to the external pyridine rings. Indeed, dihedral angles between these rings are 15.6(1)° and 12.7(1)°. The molecules pack as closely stacked (3.34 Å interplanar spacing) aromatic layers roughly parallel to the 110 plane. Once again, the two chloroform molecules of crystallization are located so that each makes close contacts with both N(2) (2.40 Å) and N(5) (2.29 Å) or N(3) (2.33 Å) and N(7) (2.35 Å), respectively.

The condensation of bis(enaminone) **3** with 2,2′-bipyridyl-6-carboxamidine (**7**) provides an opportunity to extend the number of heterocyclic units in the system. Firstly, the

Scheme 2

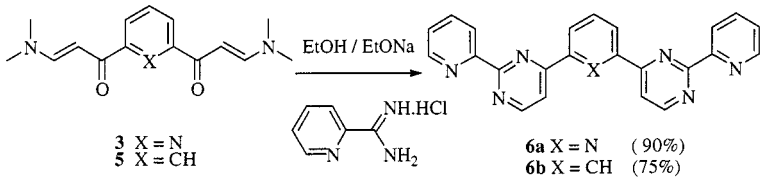
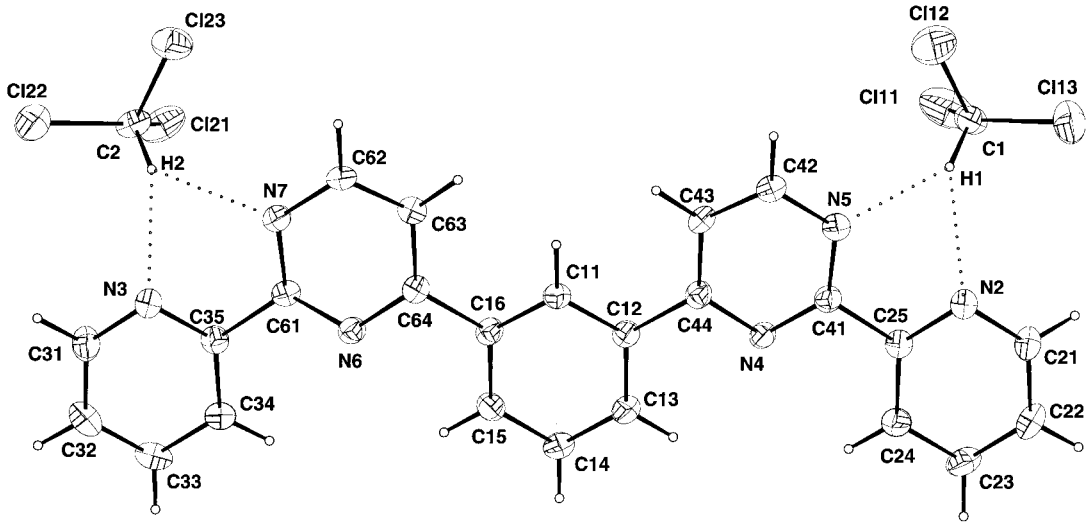
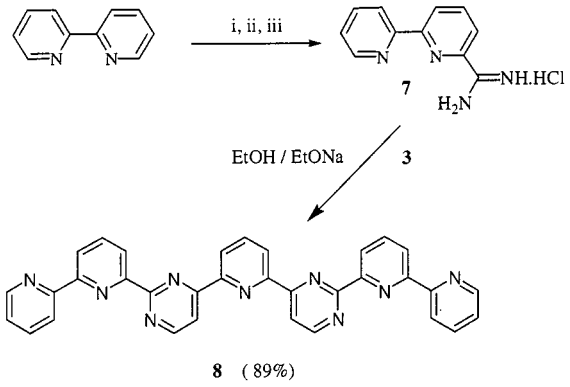


Figure 3. Molecular view of compound **6b** with atom-labelling scheme; ellipsoids represent 30% probability



carboxamidine **7** was prepared in a three-step procedure starting from the 2,2′-bipyridine (Scheme 3).

Scheme 3. i) *m*-CPBA in CH_2Cl_2, 80%; ii) Me_3SiCN, Me_2NCOCl, 66%; iii) MeOH/MeONa and NH_4Cl/EtOH, reflux, 100%

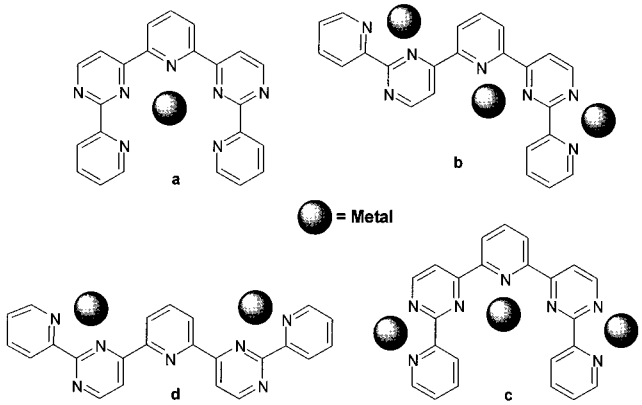


8 (89%)

The 2,2′-bipyridine *N*-oxide, prepared in 80% yield using *meta*-chloroperbenzoic acid (*m*-CPBA) under known conditions,[7] was transformed into the 6-cyano-2,2′-bipyridine in 66% yield according to the procedure described by Fife.[12] The conversion of this material to the 2,2′-bipyridyl-6-carboxamidine (**7**) was achieved in quantitative yield using literature conditions.[13] The polyaza-heterocyclic structure **8** (Scheme 3) was obtained in excellent yield (89%) by the reaction of **3** with 3 equivalents of **7** and 4 equivalents of sodium ethoxide in refluxing absolute ethanol.

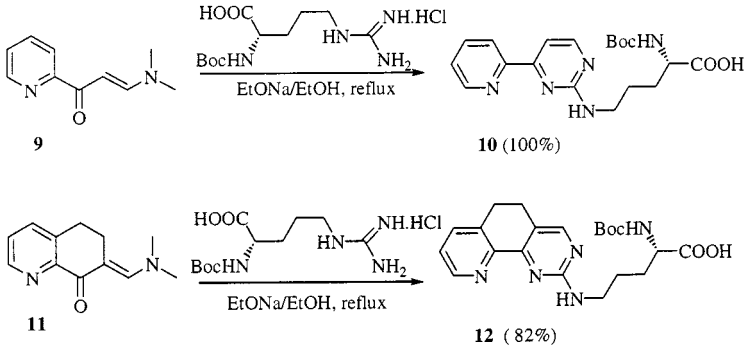
Modification of the enaminone and/or the carboxamidine or guanidine reagents, resulted in the variation of the number of nitrogen heterocycles in the final products. It should be noted that these polyaza structures may be prepared in large scale. These new multidentate ligands may bind to a metal in a variety of ways (Figure 4). Hybrid ligand **6a**, that assumes a quasi-transoid conformation in the solid state, is capable of acting as a planar pentadentate ligand to coordinate to a single metal cation **a**, or as a tris-(bidentate) ligand to coordinate to three metal cations **b**, or as a bis(bidentate) and a mono(tridentate) ligand **c**, or as a bis(bidentate) ligand **d**.

Figure 4. Different possibilities of coordination for the hybrid ligand **6a**

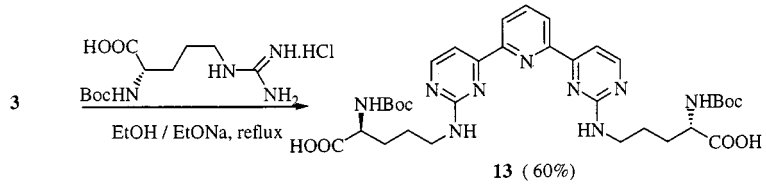


Functionalized amino acids with metal-binding sites are attractive building blocks for the construction of synthetic peptides.[14] Since there are only a few examples of functionalized amino acids with 2,2′-bipyridine or 1,10-phen-

Scheme 4



Scheme 5



anthroline fragments described in the literature,[15] we thought that it could be interesting to use this straightforward procedure in the preparation of a new functionalized amino acid using N_α-Boc-L-arginine as the guanidine reagent (Scheme 4). Reaction of enaminone **9** with 1.25 equivalents of N_α-Boc-L-arginine in the presence of 2 equivalents of sodium ethoxide in boiling ethanol resulted in the formation of 2-substituted 4-(2-pyridyl)pyrimidine **10** in quantitative yield. In this case, the reaction was complete after 6 hours, and the desired product was obtained without loss of the Boc protecting group.

As shown in Scheme 4, a ring-annulated pyridylpyrimidine may also be obtained by this method. Thus, the condensation of the 7-[(dimethylamino)methylidene]-5,6,7,8-tetrahydro-8-oxoquinoline (**11**)[6] with 1.25 equivalents of N_α-Boc-L-arginine, under the conditions described for **10**, yielded the ethano-bridged pyridylpyrimidine **12** in 82% yield. Using the bis(enaminone) **3** in the reaction with N_α-Boc-L-arginine serves as an opportunity to extend the number of heterocyclic units in a system which contains two stereogenic centres. In this case, the reaction of **3** with 3 equivalents of N_α-Boc-L-arginine in the presence of 5 equivalents of sodium ethoxide in refluxing ethanol (for 16 hours) led to the formation of the desired C_2-symmetric ligand **13** in 60% isolated yield (Scheme 5).

In conclusion, we have found that the reaction of the enaminones **3**, **5** and **9** with carboxamidines or guanidines is a versatile procedure for the preparation of a wide variety of polyaza heterocyclic structures which are of interest as building blocks for the assembly of supramolecular coordination compounds. The coordination chemistry of the new ligands and the properties of their complexes are currently under investigation, and will be the subject of further reports.[16] It is hoped that future work will allow us to generalize our synthetic method to the preparation of different functionalized amino acids with polydentate metal-binding sites.

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Experimental Section

General: All reactions were carried out under argon. − ^{1}H and ^{13}C NMR: Bruker AM-250 (250 MHz) and AC-200 (200 MHz), chemical shifts are reported in ppm downfield from Me_4Si. − All melting points are uncorrected. − CI MS and FAB MS (*m*-nitrobenzyl alcohol matrix): Quadrupolar Nermag R10-10H instrument. − Elemental analyses: LCC (Laboratoire de Chimie de Coordination) Microanalytical Service. − Column chromatography purifications: Merck alumina (70−230 mesh ASTM), deactivated with 8% water.

2,6-Bis[2-(ethylamino)-4-pyrimidyl]pyridine (**4d**)**:** A solution of *N*-ethylcarboxamidine hydrochloride (0.25 g, 3 mmol) in abs. EtOH (10 ml) was added to a stirred solution of **3** (0.3 g, 1 mmol) in boiling abs. EtOH (5 ml), and stirring was continued for 20 min. To this mixture was added sodium (0.112 g, 5 mmol) in abs. EtOH (5 ml) and the mixture was refluxed for 16 h. The solution was allowed to cool to room temperature and the black precipitate which formed was removed by filtration. The filtrate was concentrated under reduced pressure to a minimum, and then the desired product **4d** precipitated as white powder. **4d** was isolated by filtration of the white powder, which was washed with cooled ethanol, and dried to give 0.33g; yield: 95%; m.p. > 350°C − ^{1}H NMR (CD_3OD, 250 MHz): δ = 8.59 (d, 2 H, *J* = 7.9 Hz), 8.2 (dd, 1 H, *J* = 8.5, 8.6 Hz), 7.7 (d, 2 H, *J* = 4.6 Hz), 7.4 (d, 2 H, *J* = 8.5 Hz), 3.6 (m, 4 H), 1.3 (t, 6 H, *J* = 7.2 Hz) − ^{13}C NMR (CD_3OD): δ = 162.5, 159.6, 153.9, 138.7, 122.2, 105.6, 30.4, 26.2, 14.8. − $C_{17}H_{19}N_7$(321.38): calcd. C 63.53, H 5.96, N 30.51; found C 63.82, H 5.85 N 30.18 − MS; *m*/*z* (%): 322 (100) [MH^+].

Bis(enaminone) **5**: To 2,6-diacetylbenzene (3.24 g, 20 mmol), was added *N*,*N*-dimethylformamide dimethylacetal (10.6 ml, 80 mmol,

4 equiv.). The reaction mixture was then heated at 100°C for 16 h. After concentration of the solution under reduced pressure, 5.4 g (99% isolated yield) of **5** was obtained by crystallization from THF/Et_2O; m.p. 170−172°C. − IR (KBr): $\tilde{\nu}$ = 1646 cm^{-1} (CO). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 8.4 (s, 1 H), 7.99 (dd, 2 H, *J* = 7.5, 7.5 Hz), 7.82 (d, 2 H, *J* = 12.33 Hz), 7.46 (t, 1 H, *J* = 7.76 Hz), 5.78 (d, 2 H, *J* = 12.34 Hz), 3.15 (s, 6 H), 2.94 (s, 6 H). − ^{13}C NMR ($CDCl_3$): δ = 188.2, 154.3, 140.3, 129.8, 127.9, 126.3, 92.0, 45.3, 37.2. − $C_{16}H_{20}N_2O_2$(272.34): calcd. C 70.56, H 7.40, N 10.29; found C 70.12, H 7.65, N 10.21. − MS; *m*/*z* (%): 273 (100) [MH^+].

2,6-Bis[2-(2-pyridyl)-4-pyrimidyl]pyridine (**6a**): To a stirred solution of **3** (1.0 g, 3.6 mmol) in hot abs. EtOH (10 ml), was added 2.5 equiv. of 2-pyridinecarboxamidine in abs. EtOH (10 ml), followed by the addition of sodium ethoxide, prepared from sodium (0.331g, 14.4 mmol, 4 equiv.) and abs. EtOH (15 ml). After refluxing for 16 h, the mixture was allowed to cool to room temperature and concentrated under reduced pressure. The desired product **6a** was purified by column chromatography on deactivated alumina (CH_2Cl_2/EtOAc, 8:2); yield: 1.26 g (90%); m.p. > 350°C. − ^1H NMR (CD_3OD, 250 MHz): δ = 9.18 (d, 2 H), 9.01 (d, 2 H), 8.86 (d, 2 H), 8.8 (d, 2 H), 8.76 (d, 2 H), 8.3 (dd, 1 H), 8.1 (td, 2 H), 7.63 (m, 2 H). − ^{13}C NMR (CD_3OD): δ = 164.1, 163.9, 160.0, 155.4, 154.5, 150.5, 139.9, 138.9, 126.7, 125.1, 125.0, 117.8. − $C_{23}H_{15}N_7$(389.41): calcd. C 70.94, H 3.88, N 25.18; found C 71.09, H 4.06, N 24.85. − MS; *m*/*z* (%): 390 (100) [MH^+].

2,6-Bis[2-(2-pyridyl)-4-pyrimidyl]benzene (**6b**): To a stirred solution of **5** (2.72 g, 10.0 mmol) in hot abs. EtOH (50 ml) was added 3 equiv. of 2-pyridinecarboxamidine (4.73 g, 30.0 mmol) in abs. EtOH (100 ml), followed by the addition of 5 equiv. of sodium ethoxide prepared from sodium (1.15 g, 50.0 mmol) and abs. EtOH (50 ml). After refluxing for 16 h, the mixture was allowed to cool to room temperature and the formed precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to a minimum and then the white precipitate appeared. The desired product was isolated by filtration to give, after washing with cooled ethanol and drying, 2.93 g (75%) of **6b**; m.p. > 350°C. − ^1H NMR (CD_3OD, 250 MHz): δ = 9.16 (s, 1 H), 8.95 (t, 2 H), 8.81 (dd, 2 H), 8.75 (dd, 2 H), 8.53 (dd, 2 H), 8.09−8.0 (m, 4 H), 7.81 (t, 1 H), 7.57 (m, 2 H). − ^{13}C NMR (CD_3OD): δ = 164.2, 163.7, 159.4, 155.4, 150.4, 138.7, 137.6, 130.9, 130.5, 126.9, 126.6, 125.0, 117.2. − $C_{24}H_{16}N_6$(388.42): calcd. C 74.21, H 4.15, N 21.64; found C 74.60, H 4.06, N 21.35. − MS; *m*/*z* (%): 389 (100) [MH^+].

2,2′-Bipyridyl-6-carboxamidine (**7**): This material was prepared and isolated in quantitative yield upon treatment of 6-cyano-2,2′-bipyridine with sodium methoxide and ammonium chloride according to Singh[9]; m.p. 185−188°C. − ^1H NMR (CD_3OD, 250 MHz): δ = 8.76 (d, 1 H), 8.7 (d, 1 H), 8.5 (d, 1 H), 8.29 (dd, 1 H), 8.25 (dd, 1 H), 8.0 (t, 1 H), 7.53 (m, 1 H). − ^{13}C NMR (CD_3OD): δ = 161.9, 155.7, 153.6, 149.5, 143.5, 139.6, 137.6, 125.2, 124.9, 123.6, 122.0. − MS, *m*/*z* (%): 199 (100) [MH^+].

2,6-Bis[2-(6-bipyridyl)-4-pyrimidyl]pyridine (**8**): To a hot solution of **3** (1.0 g, 3.6 mmol) in abs. EtOH (10 ml), was added 3 equiv. of 2,2′-bipyridyl-6-carboxamidine (**7**) in abs. EtOH (10 ml), followed by the addition of 4 equiv. of sodium ethoxide (0.33 g of sodium in 10 ml of abs. EtOH). The mixture was refluxed for 16 h, then allowed to cool to room temperature, and the precipitate was removed by filtration. The desired product was obtained in 89% yield (1.74 g) by recrystallization from dichloromethane/ethyl acetate; m.p. > 350°C. − ^1H NMR (CD_3OD, 250 MHz): δ = 8.9 (d, 4 H), 8.8 (dd, 4 H), 8.56 (d, 4 H), 8.4 (dd, 1 H), 8.1 (m, 4 H), 7.6 (m, 4 H). − ^{13}C NMR (CD_3OD): δ = 164.2, 157.9, 155.5, 150.7, 145.0, 140.9, 139.3, 127.0, 126.5, 124.1, 123.6. − $C_{33}H_{21}N_9$(543.58): calcd. C 72.92, H 3.89, N 23.19; found C 73.14, H 3.71, N 23.45. − MS; *m*/*z* (%): 544 (100) [MH^+].

2-{BocHNCH(CO₂H)[CH₂]₃HN}-4-(2-pyridyl)pyrimidine (**10**): To a stirred solution of **9** (0.5 g, 2.8 mmol) in boiling abs. EtOH (17 ml) was added a solution of N_α-Boc-L-arginine (0.96 g, 3.5 mmol, 1.25 equiv.) in abs. EtOH (10 ml). After 10 min, of stirring, sodium ethoxide (from 0.13 g, 5.6 mmol, 2 equiv. of sodium and 6 ml of abs. EtOH) was added, and the reflux maintained for 6 h. The solution was cooled to room temperature, and concentrated under vacuum. The residue was purified by column chromatography on deactivated alumina (methanol/diethyl ether, 97:3) to give **10** (1.1 g, 100%) as a white powder; m.p. 115−117°C; $[\alpha]_D^{25}$ = +13.5 (*c* = 1.0, CH_3OH). − ^1H NMR ($CDCl_3$, 250 MHz): δ = 8.6 (d, 1 H), 8.27 (d, 1 H), 7.7 (dd, 1 H), 7.4 (d, 1 H), 7.3 (m, 1 H), 6.5 (m, 3 H), 5.9 (d, 1 H), 4.1 (s, 1 H), 3.4 (m, 2 H), 1.7 (m, 4 H), 1.3 (s, 9 H). − ^{13}C NMR ($CDCl_3$): δ = 178.1, 163.9, 161.7, 157.3, 156.0, 154.2, 149.1, 136.8, 125.0, 121.6, 106.0, 79.1, 52.0, 50.3, 30.3, 28.3, 25.8. − $C_{19}H_{25}N_5O_4$(387.43): calcd. C 58.9, H 6.5, N 18.08; found C 58.21, H 6.35, N 17.74. − MS; *m*/*z* (%): 388 (100) [MH^+].

2-{BocHNCH(CO₂H)[CH₂]₃HN}-5,6,7,8-tetrahydro-3-aza-1,10-phenanthroline (**12**): This compound was prepared according to the procedure described for **10**. The reaction of **11** (1.0 g, 4.9 mmol) with 1.25 equiv. of N_α-Boc-L-arginine and 2 equiv. of sodium ethoxide in boiling abs. EtOH gave 1.64 g (82%) of **12** as a pale yellow crystalline powder after workup and purification by column chromatography on silica gel (methanol); m.p. 120−125°C; $[\alpha]_D^{25}$ = +16 (*c* = 1.0, CH_3OH). − ^1H NMR (CD_3OD, 250 MHz): δ = 8.6 (d, 1 H), 8.3 (s, 1 H), 7.7 (d, 1 H), 7.4 (dd, 1 H), 4.8 (m, 3 H), 4.1 (s, 1 H), 3.4 (m, 2 H), 3.0 (d, 2 H), 2.9 (d, 2 H), 1.9 (m, 4 H), 1.4 (s, 9 H). − ^{13}C NMR (CD_3OD): δ = 177.5, 161.6, 158.1, 156.8, 155.8, 149.1, 147.7, 136.6, 135.8, 124.9, 117.8, 78.7, 54.5, 40.5, 29.8, 27.5, 26.8, 24.5, 22.3. − $C_{21}H_{27}N_5O_4$ (413.47): calcd. C 61.00, H 6.58, N 16.94; found C 61.22, H 6.45, N 16.78. − MS; *m*/*z* (%): 414 (100) [MH^+].

2,6-Bis(2-{BocHNCH(CO₂H)[CH₂]₃HN}-4-pyrimidyl)pyridine (**13**): To **3** (1.2 g, 4.2 mmol) in a solution of hot abs. EtOH (15 ml) was added a solution of N_α-Boc-L-arginine (3.46 g, 12.6 mmol, 3 equiv.) in abs. EtOH (30 ml), followed by the addition of sodium (0.484 g, 21.0 mmol, 5 equiv.) in abs. EtOH (40 ml). The mixture was refluxed for 6 h. The solution was then concentrated under reduced pressure and the residue was purified by column chromatography on deactivated alumina (methanol/aqueous ammonia; 9:1) to give 1.8 g of **13** as a beige powder (yield: 60%); m.p. 130−135°C; $[\alpha]_D^{25}$ = +8.3 (*c* = 1.0, CH_3OH). − ^1H NMR (CD_3OD, 250 MHz): δ = 8.5 (d, 2 H), 8.4 (d, 2 H), 8.1 (dd, 1 H), 7.7 (d, 2 H), 5.1 (m, 6 H), 4.1 (s, 2 H), 3.5 (m, 4 H), 1.9 (m, 8 H), 1,5 (s, 18 H). − ^{13}C NMR (CD_3OD) δ = 176.3, 163.0, 161.3, 157.4, 155.7, 153.0, 137.2, 122.1, 105.5, 78.6, 53.8, 40.2, 29.4, 27.3, 24.7. − $C_{33}H_{45}N_9O_8$(695.77): calcd C 56.97, H 6.52, N 18.12; found C 56.63, H 6.18, N 17.96. − MS (CH_3OH, HCO_2H); *m*/*z* (%): 696 (100) [MH^+].

X-ray Crystallographic Study: Data for **6a** were collected at room temperature with an Enraf-Nonius CAD4 diffractometer whereas for **6b**, they were collected with a Stoe IPDS diffractometer at 160 K. The final unit-cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections for **6a** and 5000 reflections for **6b**. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections. The two structures were solved by direct methods (SIR92[17]) and refined by least-squares procedures on F^2. All H atoms attached to carbon atoms were introduced in calculation in idealized positions

[d(C−H) = 0.96 Å] and treated as riding models with isotropic thermal parameters 20% higher than those of the carbon atom to which they are attached. Least-squares refinements were carried out by minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ models reached convergence with $R = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$, having values listed in Table 1. The calculations were carried out with the SHELXL-97 program[18] running on a PC. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101840 (**6a**), -101841 (**6b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data

	6a	**6b**
Empirical formula	$C_{25}H_{17}Cl_6N_7$	$C_{26}H_{18}Cl_6N_6$
Molecular mass [g mol^{-1}]	628.16	627.16
Crystal size [mm]	0.87, 0.15, 0.10	0.43, 0.30, 0.10
Crystal system	tricyclic	tricyclic
Space group	*P*1	*P*1
a [Å]	11.402(2)	7.366(1)
b [Å]	10.42(2)	13.357(3)
c [Å]	15.804(8)	14.605(3)
α [Å]	81.48(9)	78.44(3)
β [Å]	73.79(4)	81.54(3)
γ [Å]	87.26(9)	79.40(3)
V [Å^3]	1395(3)	137.(5)
Z	2	2
F(000)	636	638
ρ(calcd.)[g cm^{-3}]	1.495	1.515
μ (Mo-K_α) [mm^{-1}]	0.645	0.654
Diffractometer	Enraf-Nonius CAD4	Stoe IPDS
Radiation	Mo-K_α (λ = 0.71073)	Mo-K_α (λ = 0.71073)
T [°K]	293	160
Scan mode	ω/2θ	φ (rotation)
2θ range [°]	4 < 2θ < 46	3.8 < 2θ < 48.54
No. of rflns. collected	4136	11011
No. of unique reflns. [*R*(int)]	3885 (0.047)	4074 (0.046)
Reflections used [$I > 2\sigma(I)$]	1107	3260
R,*R* (all data)	0.0475, 0.2181	0.0341, 0.0473
wR^2, wR^2 (all data)	0.1125, 0.1555	0.0797, 0.0857
$(\Delta/\sigma)_{max}$	0.041	0.024
$\Delta\rho_{min}/\Delta\rho_{max}$	−0.253/0.248	−0.230/0.305
GOF	0.819	0.025
Variable parameters	343	343

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